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Synthesis of lanthanum manganites by combustion method from starch-based precursors

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Lanthanum manganite powders with perovskite structure were obtained by combustion method from starch-based precursors and metal nitrates. The interaction of lanthanum and manganese ions with starch was analysed by infrared spectroscopy. The combustion reactions were studied by thermal analysis. The as-synthesised powders, as well as the annealed samples were characterised by X-ray diffraction and specific surface area measurements (B.E.T. method). The influence of the fuel (starch)/oxidiser (metal nitrates) molar ratio and the annealing temperature on the structure and morphology of the samples were investigated.

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1. Introduction

The morphology of the perovskite oxides depends on the synthesis procedure, which makes it necessary to perform systematic studies on the synthesis parameters [1,2]. For obtaining perovskite materials, “soft chemistry” routes were developed as colloidal crystal templating method [3], flame hydrolysis [2], Pechini process using citrates or polymeric precursors [1], w/o microemulsion [4], combustion method [5-7], etc.

The combustion method is one of the simplest and cheapest techniques for obtaining nanocrystalline ceramic materials. The combustion synthesis could be controlled by the fuel (organic compound) /oxidising agent (metal nitrates) ratio [8] from Smoldering Combustion Synthesis (SCS) when the oxidising agent is in excess, to Volume Combustion Synthesis (VCS) when the reagents are approximately in stoichiometric proportions (according the propellants rule), or to Self-propagating High-temperature Synthesis (SHS) when the fuel is in excess. In the VCS mode, the contamination of the product with unburned fuel could be avoided, but the energy is released very fast and the reaction could get explosive character. The most suitable for materials synthesis is the SHS mode when a reaction wave is formed and the temperatures are high enough to form a crystalline powder. The residual carbon formed in the SHS mode could be removed by annealing as-synthesised powders in air with an increasing of crystalline degree.

The obtaining of lanthanum manganite powders was reported for the combustion of citric acid [9], glycine [8], urea [10], or other fuel based-precursors. Since now, only chemical modified starch is mentioned for obtaining of perovskite type materials [11,12]. In this paper we report the synthesis and characterisation of lanthanum manganite by combustion method using commercial soluble potato starch as fuel.

2. Experimental

The chemicals, $La(NO_3)_3 \cdot 9H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ (Fluka, 99%), and starch (Acros) were used as received. The quantities of starting substances were calculated to obtain 4 mmols lanthanum manganite. The stoichiometric combustion ratio was determined using the total reducing valence of the fuel (starch) and the total valence of oxidisers (metal nitrates) according to the propellants rule.

Each reaction mixture was dissolved in 20 mL deionised water in Pyrex beakers, heated on a hot plate to obtain a viscous liquid, then kept overnight in a drying oven at 60°C to evaporate the water and to obtain the precursors. Two combustion regimes have been tested volume combustion (10% fuel excess from stoichiometry, $\varphi = 1.1$) and self-sustained combustion (40% fuel excess from stoichiometry, $\varphi = 1.4$). The combustion was performed in Pyrex beakers in a preheated furnace at 350°C. The resulted as-synthesized powders were calcined in air, at 700 °C, 6h to remove residual carbon and to improve the crystalline structure. The FT-IR spectra were recorded on a Nicolet Magna IR Spectrometer 550 in the range 400 - 4000 cm^{-1}. The ignition temperatures, as well as the weight losses were determinated by thermogravimetry on a Setaram B70 thermobalance from room temperature up to 700°C, with a heating rate of 5°C/min. The calorimetric measurements were performed on a Mettler Toledo DSC 823 in the temperature range 30°- 400°C, with a heating rate of 5°C/min. The X-ray diffraction patterns of the samples deposited on glass substrate were obtained using a Siemens D500 diffractometer with CuK_{α} radiation (λ = 1.5418 Å), at a step of 0.04°/s in the range $2\theta = 20$ to 60°. The crystallite sizes (D_{202}) were calculated by means of the Scherrer's equation, $D = 0.9\lambda/\beta \cos\theta$, where λ is the wavelength of the X-ray used, and β, the full width at half-maximum

(FWHM) of the X-ray reflection ($2\theta = 46.72$). The specific surface areas were measured by nitrogen adsorption-desorption at liquid nitrogen temperature (BET method).

3. Results and discussions

In the combustion method, the fuels are also chelating agents, which contain carboxyl, carbonyl or amine groups. Polysaccharides coordinate to metal atoms with involvement of the lone electron pair orbitals of the hydroxyl groups. Potato starch forms Werner-type complexes with acetate, chlorides and nitrates of some transition metals like, Mn^{2+}, Cu^{2+}, Co^{2+}, etc. [13, 14]. In certain condition La^{3+} ions could also form complexes with starch [15].

The isolated starch-based precursors of lanthanum manganite were investigated by FT-IR spectra and thermal analysis. The FT-IR spectrum of starch-based precursor shows the characteristic vibration modes of nitrate ion (ν_2 = 815 cm^{-1}, ν_3 = 1385 cm^{-1} and ν_4 = 738 cm^{-1}). The bands at 1165 cm^{-1} (δ_{OH}), 1653 cm^{-1} (ν_{CO}) and 3436 cm^{-1} (ν_{OH}) in the FT-IR spectrum of starch are shifted toward lower frequencies, 1155 cm^{-1} 1642 cm^{-1} and 3425 cm^{-1} in starch-based precursor, respectively (Fig. 1). It could assume that metal cations are bounded to oxygen atom of some hydroxyl groups of D-glucose units of starch, forming a kind of clathrates [14], in which significant amount of water might be retained.

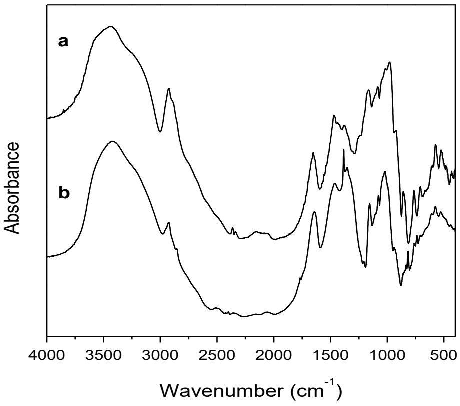


Fig. 1. FTIR spectra of starch (a) and starch-based precursor (φ = 1.4) of lanthanum manganite (b).

In the thermal analysis of starch-based precursors of lanthanum manganite (Fig. 2), the endothermic process from 100° – 140 °C could be assigned to the loss of water retained in the gel, followed by the decomposition of starch with forming dextrins. These intermediary products might react with metal cations by complexation [16]. One can notice that the ignition temperature is very similar for both precursors (Table 1) and some decomposition steps occur before the combustion. The exothermic effect from 250° - 285 °C corresponds to the burning of residual carbon reach compounds and is continued to higher temperatures. The combustion could be considered finished at 600 °C for both samples.

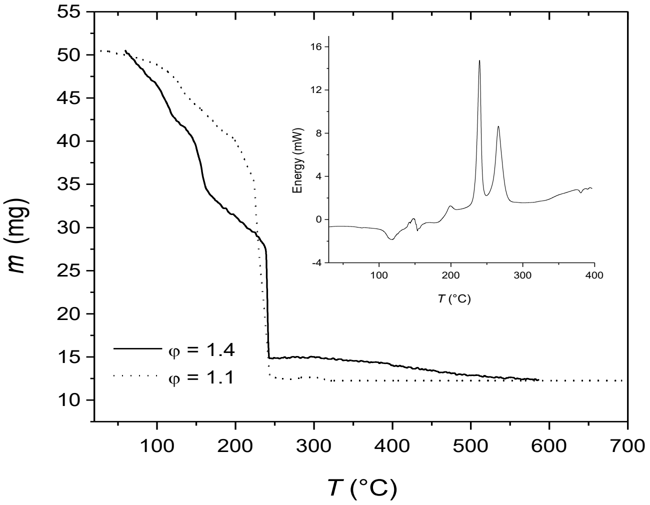


Fig. 2. TG curves for La-Mn-starch precursors (inset, the DSC curve for φ = 1.4).

Table 1 lists the obtained phases proved from XRD patterns, specific surface areas values and the ignition temperature for samples of φ = 1.1 and φ = 1.4. The as-synthesised sample, at φ = 1.1 is an amorphous compound, whereas after annealing, single phase $LaMnO_{3.15}$ with orthorhombic structure (JCPDS 89-0680) was obtained. The specific surface areas values of both calcined samples are similar.

Table 1. Properties of investigated systems.

φ	Ignition temperature (°C)	As- synthesized powders		Calcined powder (700°C, 6h)	
		Obtained phase	*S* (m^2/g)	*Obtained phase*	*S* (m^2/g)
1.1	232	amorphous	ND*	$LaMnO_{3.15}$	16.3
1.4	238	$La_{1-x}Mn_{1-z}O_3$	24.1	$La_{1-x}Mn_{1-z}O_3$	17.8

*ND – not determined

In order to study the influence of calcining temperature on the sample structure, a precursor prepared at φ = 1.4 was ignited in air and then, progressively annealed in a preheated furnace at 125 °C, 250 °C, 450 °C, 650 °C and 800 °C, 1h for each temperature (Fig. 3.). From XRD patterns of the samples, it could notice that the crystallinity decreases from room temperature to 250 °C and then, increases for higher temperatures. The XRD patterns for the samples annealed at temperature up to 250 °C correspond to $La_{1-x}Mn_{1-z}O_3$ with cubic symmetry

(JCPDS 51-1516) and for samples calcined between 450° – 800 °C to $La_{1-x}Mn_{1-z}O_3$ with rhombohedral perovskite structure (JCPDS 51-1514). During the combustion, the high energy released, brings the reaction mixture at very high temperature, almost instantaneously, whereas the large quantity of evolved gases, produces a fluffy powder, which is cooled very fast at room temperature. In this way, some metastable structures could be quenched.

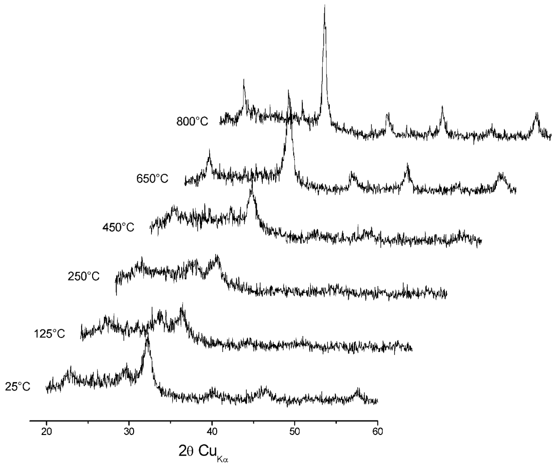
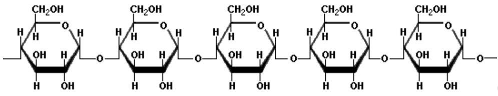
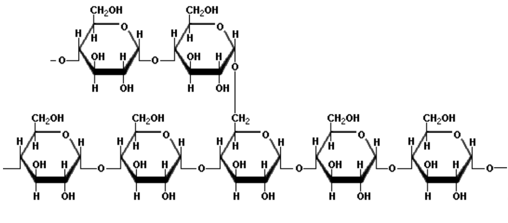


Fig. 3. XRD patterns of lanthanum manganite samples (φ = 1.4) annealed at different temperatures.

The three dimensional structure of the polymer is important and influence the morphology of lanthanum manganite powders. We have tested different commercial soluble starch from Acros, Merck and Prolabo suppliers. The iodine test revealed a different ratio of amylose (**1**) and amylopectin (**2**) of these products.


(1)


(2)

For the same synthesis parameters (φ = 1.2, ignition in air and annealing at 800°C, 1h) the precursor with starch rich in amylopectin (Acros) has been a hard, transparent gel and after calcinations, $La_{1-x}Mn_{1-z}O_3$ with rhombohedral perovskite structure, 36 nm crystallite size and specific surface area of 12 m^2/g has obtained. The precursor with starch poor in amylopectin (Prolabo) has been a viscous gel and after annealing the same structure, $La_{1-x}Mn_{1-z}O_3$, but with smaller crystallite size (20 nm) and higher specific surface area (15 m^2/g) has resulted. The sample prepared with starch from Merck has presented intermediary values for crystallite size and specific surface area.

4. Conclusions

Lanthanum manganite powders were synthesised by combustion method from starch-based precursors. The FT-IR spectra have revealed the coordination of starch to metal cations, while the thermal analysis has showed decomposition in steps of starch-based precursors. For lower fuel content, $LaMnO_{3.15}$ was obtained, whereas for higher fuel content, nonstoichiometric lanthanum manganite was formed. The annealing temperature induces structural modifications of lanthanum manganite powders from cubic to rhombohedral symmetry. The influence of amylopectin content in starch-based precursors on the morphology of the samples was noticed.

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